The Mechanism of Asphalt Formation

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DISSERTATION

SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE FACULTY OF PURE SCIENCE, COLUMBIA UNIVERSITY, IN THE CITY OF NEW YORK
JUNE, 1925

By

OTTOMAR G. STRIETER, B.A., M.A.

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TABLE OF CONTENTS

Abstract 7
Introduction 8
Origin of Asphalts 8
Earlier Studies on the Constitution of Asphalts 11
Discussion of Procedure 12
Experimental Work:
Distillation of Asphalts 13
Definition of Substances 16
Physical Constants 17
Carbon and Hydrogen 19
Effect of Distillation on the Sulphur Compounds of Asphalts 21
Classification of Chemical Constituents 22
Sulphuric Acid Test 24
Molecular Weights 26
Action of Sulphur Chloride on Asphalt Distillates:
(*a*) Qualitative 28
(*b*) Quantitative 30
(*c*) Analysis of Asphaltenes 31
(*d*) Transitions 32
(*e*) Marcusson's Method 32
(*f*) Asphalt Binder 33
(*g*) Sulphuration of Crude Petroleum 33
Summary of All Experiments 33
The Mechanism of Asphalt Formation 35
Probable Structure of Asphalts 37
Summary 38

The Mechanism of Asphalt Formation

Abstract

This research was planned and carried out for the purpose of discovering fundamental information that would throw some light upon the mechanism of asphalt formation.

A systematic study was made of three representative asphaltic materials which are used extensively in the industry.

The general procedure adopted was that of making a detailed study of the natural fractions obtained by careful distillation of each asphalt.

This study yielded results which add facts to the chemistry of asphalt formation which have heretofore not been known, and which seem to be of basic importance for further researches:

1. Physical constants, such as specific gravity, viscosity, index of refraction and molecular weight were determined on the asphalt distillates. The great similarity of the physical constants suggested that destructive distillation of the asphalts causes a depolymerization.

2. A study of the chemical properties of the distillates confirmed the depolymerization hypothesis, besides giving valuable information of the nature of the oils.

3. A study of the reaction between the oils and sulphur chloride showed some of the mechanism by which asphalts might be formed.

4. The quantitative estimation of the sulphur chloride reaction showed that this reaction is governed by the unsaturation of the hydrocarbons present. The presence of sulphur in the oil diminishes the magnitude of the reaction.

5. It is possible from the experimental data to postulate a new theory, namely, that asphalts depolymerize upon destructive distillation, and again polymerize when the distillation products are treated with sulphur chloride.

6. A new property is assigned to the asphaltic resins, namely, that as the "binder" material of asphalts. On this "binder" theory the deterioration of asphalt pavements is explained.

7. An attempt is made to explain the difference in sulphur combination in asphalts and asphaltites.

8. On the basis of solubility tests, a new method was developed for the analysis of synthetic asphaltenes.

9. A study of the molecular magnitudes of the asphalts and asphalt distillates, together with the depolymerization theory, made it possible to estimate the average number of rings present in the polycyclic asphaltic hydrocarbon molecule.

Introduction

On account of its unusual properties asphalt is used for many purposes throughout the industries. The largest quantity of this material, however, has been used in road and street construction.

The rapid development of the motor truck and the consequent increase in the use of the highway for freight transportation, has brought about a condition that makes necessary the use of a paving material that is more resistant to heavy wear than is asphalt. This development has brought to the asphalt industry a serious problem, *i. e.*, the discovery of new uses for this valuable material.

Heretofore, asphalt has been used in the crude or raw state only, or at most in only a slightly modified condition. A survey of the possible uses of raw asphalt would seem to indicate that there is little hope that the loss of tonnage in the paving industry will be met by requirements from new uses. However, practically nothing has been done toward the development of products through chemical reactions in which asphalt is the important raw material. For instance, a preliminary study seemed to indicate that one or more of the products of asphalt could be used in the production of cold moulded insulation with high dielectric properties, but before this work could be carried further, fundamental information concerning the constitution of asphalt and the mechanism of asphalt formation was needed.

A survey of the literature showed that little or nothing of fundamental importance had resulted from the empirical studies previously made. With the hope of securing some insight into the nature of the constitution of asphalt and especially of the mechanism of asphalt formation, this research was begun.

Origin of Asphalts

Asphalts are divided into two major groups, namely, natural and artificial.

The artificial asphalts include all substances which resemble natural asphalts and are obtained as still residues when certain classes of organic substances are dry distilled.

The natural asphalts are subdivided into true asphalts, asphaltites and asphaltic rocks. The latter again into asphaltic limestones and asphaltic sands.

In considering the genetic relationship between asphalt and petroleum, the following possibilities present themselves: (1) the transformation of petroleum into asphalt, (2) that of the asphalt into petroleum, and (3) the simultaneous formation of petroleum and asphalt.

According to Mabery[1] there can be no doubt but that asphalts in general have been formed from petroleum, and that in many places, as in Canada, this phenomenon may still be observed.

The opposite view was held by O. Helm,[2] who believed that petroleum was the distillation product of asphalt. This view, of course, would demand that asphalts be found deep in the earth's crust and not on top, as is actually the case. Oil with the higher gravity is always found lower down than the asphalt bitumen of a higher gravity. This formation of petroleum finds no evidence in nature.

Leonhard[3] believed that asphalts were of volcanic origin. Organic materials in the earth's crust were heated by hot volcanic rocks and were destructively distilled, forming petroleum, hydrocarbon gas, carbon dioxide and water. The distillation forced a portion of the petroleum thus formed to the earth's surface, where the lighter oils evaporated off, leaving a residue of asphalt. According to this, then, asphalts and petroleum are formed simultaneously and asphalts would simply be the heavy components of petroleum after the light oils have evaporated. This could account for some asphalt formation, but since petroleum contains large quantities of heavy fractions boiling above 200° and 300° C., this process would only produce at most very viscous asphaltic products. It could never account for the formation of very hard asphalt, such as the Trinidad Lake, with its high softening point.

The natural and simplest view for the origin of asphalts is that noticed, even now, in nature, namely, the thickening and hardening of petroleum. So it is at present generally agreed that asphalts have been formed from petroleum.

[1] *Chem.-Ztg.*, **1896,** 83.

[2] *Apoth. Ztg.*, **1901,** 563.

[3] Engler-Höfer, "Das Erdöl," Vol. I, p. 674.

One group of investigators claimed that the conversion of petroleum into asphalt was due alone to oxidation. Among these were Boussingault,[4] Endemann,[5] L. Charitschkow[6] and others.

Terreil[7] was the first to draw attention to the sulphur content of asphalt from Camboja. Later Helm[8] showed that sulphur was a constituent of all asphalts. But Kayser[9] was the first to point out that sulphur was an active agent in the formation of asphalts. He believed that the entrance of sulphur in the petroleum molecule formed the asphalt. He was led to this view because all asphalts analyzed by him contained sulphur. Furthermore, when petroleum is distilled to which sulphur has been added, hydrogen sulphide escapes and a residue remains in the still which resembles asphalt. To this reaction Kayser assigned the following equation:

$$C_xH_y + 2S = C_xH_{y-2}S + H_2S$$

Later Richardson[10] pointed out that the sulphur acted as a polymerizing agent. This view he based on his belief that asphalts consisted largely of polymerized olefines. Olefines tend toward polymerization, and so Richardson thought that sulphur acted as the polymerizing agent in the formation of asphalt.

A change of view took place when a third possibility was shown. Zaloziecki[11] proved the presence of naphthenes, naphthylenes and terpenes in petroleum. It was well known that these compounds polymerize and thus give an explanation of the formation of asphalts.

Marcusson[12] sees a parallel in the formation of coal and asphalts. The series humic acid, humines, peat, lignite, bituminous coal, anthracite, finds analogy in the series asphaltic acids, anhydrides, asphaltic resins, asphaltenes, carbenes, carboides, which last series is formed from petroleum.

For reasons which need not be stated in detail, it is very probable that all these factors, namely, oxidation, polymerization, condensation and sulphuration, have taken part in the formation

[4] *Ann. chim. phys.*, **64,** 17, 73 and 442.
[5] *Jour. Soc. Chem., Ind.* **17,** 1003.
[6] *Chem.-Ztg.*, **1908,** Rep. 5.
[7] *Jahresber. Chem.*, **1864,** 869.
[8] *Arch. Pharm.*, **8,** 1877; **10,** 1878.
[9] Engler-Höfer, "Das Erdöl," Vol. I, p. 677.
[10] *Chem.-Ztg.*, **1897,** 289.
[11] *Dinglers polytech. J.*, **293,** 114.
[12] *Chem.-Ztg.*, **1920,** No. 6, p. 43.

of asphalts from petroleum. A number of investigators have suggested one or more of these actions as the possible means of asphalt formation, but not one has offered experimental evidence to support such claims.

Earlier Studies on the Constitution of Asphalts

Natural asphalts consist of bitumen and mineral matter. The mineral matter is considered an impurity. The bitumen forms the real asphalt content. All bitumen of asphalts contains carbon, hydrogen, sulphur; to some extent oxygen and small quantities of nitrogen.

Clifford Richardson[13] separated asphalt into different groups of components by treating successively with different solvents, such as carbon disulphide, carbon tetrachloride and petroleum naphtha.

Marcusson[14] divides the components of asphalts into five major groups, namely: unchanged petroleum, neutral petroleum resins, asphaltenes, asphaltic acids and their anhydrides. This procedure constituted a distinct advance in the chemistry of asphalts; it has the advantage that it classifies the components of asphalts into distinct chemical groups. Marcusson has also shown that asphalts are saturated cyclic compounds.

Some asphaltites,[15] such as Grahamite and Gilsonite, contain carbenes. Carbenes are the components which are insoluble in carbon tetrachloride, but soluble in carbon disulphide. Carboides are, like coal, insoluble in all solvents and form the largest component of Albertite.

Kayser isolated by means of selective solvents three kinds of sulphur compounds which he named, respectively, alpha, beta and gamma asphalt. The latter alone is sensitive to light.

Jacques Errera[16] ultra-filtered the asphaltenes and found that they were largely colloidal. He also found that the sulphur compounds which were sensitive to light were in colloidal dispersion. Due to their light sensitiveness asphalts are used in photography.

The products of destructive distillation of asphalt from Val de Travers were investigated by Völckel.[17] The brown colored crude oil was washed with potassium hydroxide and then steam distilled. After washing the distillate with concentrated sul-

[13] Richardson, "The Asphalt Pavement," New York, 1908.

[14] *Z. angew. Chem.*, **1916**, p. 346.

[15] Marcusson, "Die Natürlichen und Künstlichen Asphalte," **1921**, p. 26.

[16] *Trans. Faraday Soc.*, **19**, 314–317 (1923).

[17] *Ann. Chem. Pharm.*, **87**, 139 (or Engler-Höfer, "Das Erdöl," Vol. I, p. 697).

phuric acid, it was fractionally distilled. Upon analysis the different fractions gave the same percentage composition, for which the formula C_6H_{10}, likewise $n(C_6H_{10})$ is calculated.

Similar results were obtained by Delachanal[18] in the distillation of an asphalt from the Dead Sea with a sulphur content of about 3%. At first large quantities of hydrogen sulphide and gaseous products were evolved, while a dark oil distilled over. The dark oil upon redistillation gave a colorless distillate with a boiling range of 360° C., and was similar to the distillation products of petroleum.

R. Kayser[19] fractionally distilled Syrian asphaltite and obtained ten fractions. From a determination of the carbon, hydrogen and sulphur content of the various fractions he assigned chemical formulae to the compounds, such as $C_{40}H_{68}S$ to $C_{36}H_{56}S$. Assigning formulae is of course not justifiable, because the various fractions are not individual compounds. In spite of the great differences in the sulphur content of the different fractions, one atom of sulphur is assigned to all the formulae.

Asphalts are of very complex constitution. Although many investigations have been carried on, the knowledge of the mechanism of asphalt formation is very empirical and the problem of the constitution of asphalt remains unsolved.

Discussion of Procedure

When Richardson devised his procedure of separation of asphalt constituents by means of solvents, much hope was placed upon this method.[20] It was believed that all future investigations would have to be done by means of fractional solution. The trouble with Richardson's method is that it tells nothing about the chemical identity of the different groups.

Marcusson's[21] method allows complete separation of asphalts into definite chemical groups. These definite chemical groups are of a very complex order, and so to work with them again offers great difficulties. It therefore seemed desirable to try a different method of attack than that of solvent action. The only method that presented itself was that of distillation.

Distillations of asphalts and conclusions as to their constitution have often been reported in the literature. A glance at the results will show the imperfections of the work. Thus from

[18] *Compt. rend.*, **97**, 491.

[19] Engler-Höfer, "Das Erdöl," Vol. I, p. 698.

[20] Köhler-Graefe, "Die Chemie u. Technologie d. Natürlichen u. Künstlichen Asphalte," p. 93, 2d ed. (1913).

[21] *Z. angew. Chem.*, **1916**, p. 346.

the ultimate analysis of the distillates conclusions were drawn as to the constitution of the asphalt constituents and chemical formulae were assigned. Such methods of procedure must of course be rejected.

Due[22] to the faulty conclusions in the distillation experiments and to the fact that asphalts largely decompose upon distillation, it has been held that a study of the distillation products could lead to no definite information as to the constitution of asphalts.

Nevertheless, it was believed, since Marcusson has shown that asphalts are of a polycyclic nature, that distillation might largely depolymerize asphalts so that a study of the distillation products would lead to some valuable information, and that in spite of decomposition some conclusions could be drawn as to the nature of asphalts. Then, too, it was believed that if depolymerization took place, the distillates could again be polymerized into asphalt. All our knowledge of petroleum is based on distillation, and it is well known that the petroleum compounds largely decompose upon distillation. The same is true of coal and lignite, yet great industries were built upon our knowledge of their distillation products. And then, too, our knowledge of asphalts has been increased through the investigations of Marcusson since the above-mentioned distillations of Völckel and Kayser were made.

In the present research the problem of the constitution of asphalts was studied from the products of destructive distillation.

Experimental Work

Distillation of Asphalts

The distillation was carried out in a steel still, using a glass still-head to which was attached a strong glass tube about 32 inches long as air condenser. To this air condenser a Liebig condenser was attached which was cooled with water. A thermocouple was used to measure the temperature of the vapor. This thermocouple was standardized against a standard thermometer under conditions of experiment.

The still was made by welding a bottom and flange on a steel pipe. The cover had one hole to hold the glass still-head, and was fastened to the still by means of thumbscrews. The still had an inside diameter of 5 inches and a depth of 7 inches. The thermocouple was placed in a brass tube to protect it from the

[22] Marcusson, "Die Natürlichen und Künstlichen Asphalte," p. 36.

vapors. A gasket of thin asbestos paper was used to keep the cover from leaking. Thin asbestos paper was wrapped around the bottom of the still-head until it fitted snugly in the lid and was then cemented with barium sulphate-water-glass paste to prevent leaking. The still was heated directly by means of Bunsen burners. The manner in which the still was set up is shown in Plate I.

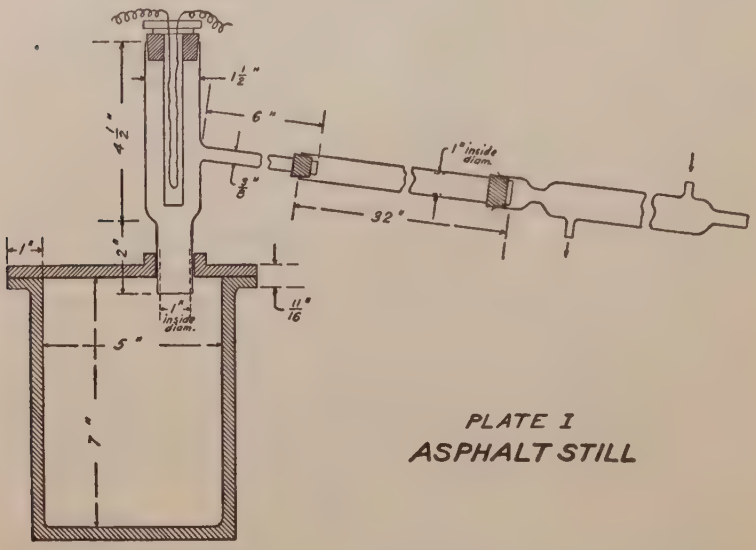


PLATE I
ASPHALT STILL

Refined Trinidad Lake Asphalt, Refined Bermudez Lake Asphalt and Gilsonite Selects were used for the distillation. These asphalts were furnished by the Barber Asphalt Company of Maurer, New Jersey. Analysis of these asphalts gave the following results:

TABLE I

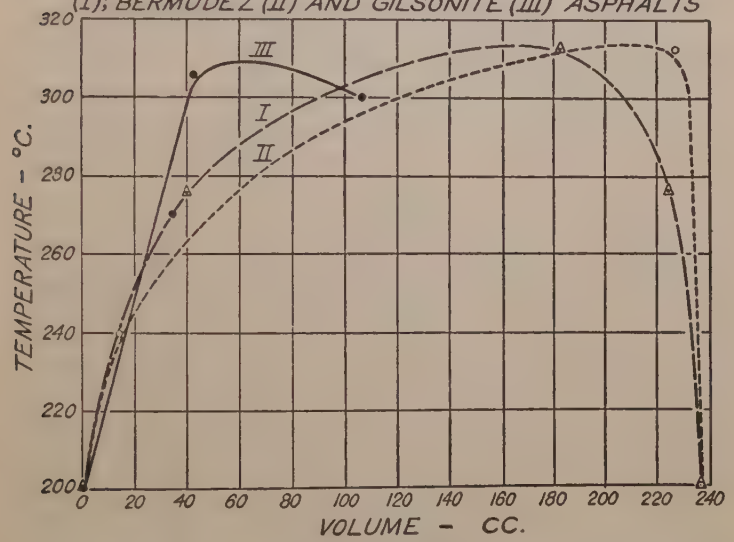
	Solubility in			Pure bitumen			
Name	CS_2 %	CCl_4 %	88° Naphtha %	Mol. wts.	Sulphur %	Carbon %	Hydrogen %
Trinidad	60.38	62.49	36.54	1131.8	4.63	74.22	8.62
Bermudez	94.65	94.28	70.15	620.4	4.16	76.75	8.68
Gilsonite	99.76	99.86	47.31	4251.5	0.78	85.63	10.45

The Trinidad and Bermudez asphalts distilled comparatively easy, but the Gilsonite showed a tendency to bump over and so was very difficult to distill. All three varieties of asphalts gave fluorescent oils and gases on distillation. The gases were in-

flammable and had the odor of hydrogen sulphide and garlic; they were condensable with ice, but were not collected. Only the oils were collected. In distilling, the temperature would rise to a maximum and then gradually drop. On the up-curve the oil that distilled over was reddish-yellow, on the down-curve deeply fluorescent. Although decomposition takes place throughout the distillation, most of the cracking takes place after the maximum temperature has been reached. Water is formed during the distillation. The Gilsonite distillate was darker (less fluorescent) than that of the other asphalts.

In redistilling the above primary distillates, no break or maximum temperature was obtained. Before distilling, the primary distillates were treated with fused calcium chloride

PLATE II – PRIMARY DISTILLATION CURVES FOR TRINIDAD (I); BERMUDEZ (II) AND GILSONITE (III) ASPHALTS



to free from the cracking water. The oils distilled with gradually rising temperature. A smooth curve was thus obtained. From this it is concluded that less cracking takes place upon redistillation than in the primary. Plates II and III show this graphically.

The temperatures of the down-curve in the primary distillation were due to cracking, giving compounds of lower boiling point. Redistillation proved this. The shape of this section of the curve may be due to some extent to the fact that the oil does not distill over fast enough to keep the temperature rising.

The color of the distillates was about the same for all of the asphalts. The first fractions were pale yellow; these gradually

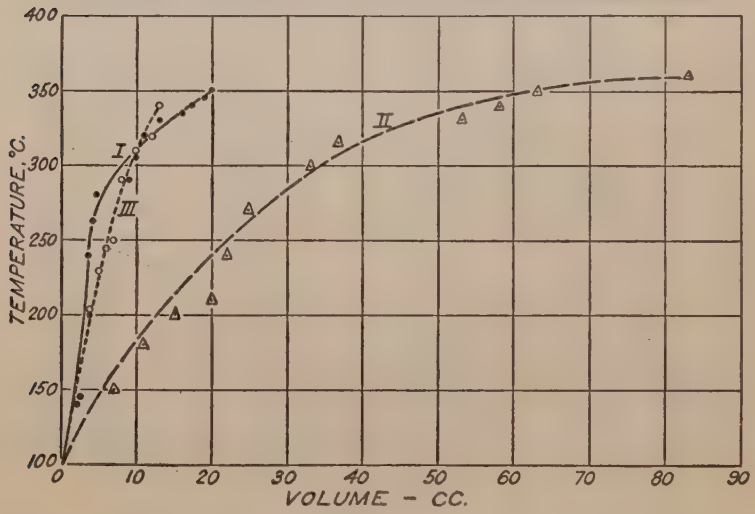
changed to red. The highest boiling or last fractions were highly fluorescent. The oils had the appearance of viscous lubricating oils.

The asphalts upon distillation produced a porous coke as residue, the quantity and nature of which, according to Richardson, is characteristic of each variety of asphalt. The above distillations confirmed Richardson's statement.

Definition of Substances

The distillates (primary) obtained by destructive distillation of the asphalts formed the substances for the further investigations of this research. Three fractions of each asphalt were obtained. The reason three fractions were made was that

PLATE III – CURVES SHOWING REDISTILLATION OF PRIMARY TRINIDAD DISTILLATES. FRACTIONS-I-II & III



the nature of the fractions changed, thus forming somewhat of a natural division.

The results tabulated below were obtained by distilling the asphalts in a 1-liter pyrex flask using a mercury thermometer to measure the temperature. The thermometer was carefully standardized by determining the boiling points of aniline, naphthalene and benzophenone. The boiling-point determinations were carried out under the same experimental conditions as the distillation of the asphalts.

Refined Trinidad Lake Asphalt.—About 400 grams of asphalt were distilled and the following fractions obtained:

Fraction	Temperature	Volume	Color
1	—— to 268°	40 cc.	Reddish
2	268° to 316° to 268°	84 cc.	Bluish fluorescent
3	268° to 200°	13 cc.	Bluish fluorescent

Refined Bermudez Lake Asphalt.—About 400 grams were distilled. Three fractions were made:

Fraction	Temperature	Yield	Color
1	—— to 240°	14 cc.	Red
2	240° to 316°	113 cc.	Fluorescent
3	316° to 200°	110 cc.	Fluorescent

Gilsonite Selects.—About 360 grams powdered Gilsonite were distilled. Three fractions were made:

Fraction	Temperature	Yield	Color
1	—— to 270°	35 cc.	Light reddish-yellow
2	270° to 306°	7 cc.	Light reddish-yellow
3	306° bumped over	65 cc.	Red

It will be seen that the different asphalts behave similarly upon destructive distillation. Conclusions as to the nature of the distillation will be given under the different experiments made on the distillates.

Physical Constants

A. Specific Gravity.—Oils have widely differing gravities, depending upon the prevalence of one kind or other hydrocarbon series and their molecular magnitude. The specific gravity is characteristic for the chemical nature of the oils. In the following the gravities were run with a 5 cc. pycnometer standardized against water. The results are found in Table II.

From the table it will be seen that the first fraction of the various asphalt distillates has the lowest gravity and the third fraction the highest. All gravities are less than 1. It will also be noticed that the Trinidad distillates show the highest specific gravities, the Bermudez distillates the next highest and those of Gilsonite the lowest.

B. Viscosity Measurement.—The viscosities were determined in an enlarged Ostwald viscosity pipette. A large glass beaker filled with water served as a thermostat. The temperature was kept constant within 0.1°; 10 cc. of oil were run into the pipette by means of a standardized pipette which delivered 10 cc. at 20°.

The Viscosity of Water.—It took water at 20° C. (about 4 cc.) 14.2 seconds to run through the capillary.

The viscosity results are recorded in Table II.

TABLE II

PHYSICAL CONSTANTS

Name	Sp. gr. at 20/20° C.	Viscosities at 20° C. against water 14.2 sec.	Indices of refraction at 20° C.
Trinidad Distillate:			
Fraction 1	0.9358	7′ 21.9″	1.5115
Fraction 2	0.9413	9′ 12.3″	1.5208
Fraction 3	0.9540	10′ 11.1″	1.5316
Bermudez Distillate:			
Fraction 1	0.9090	2′ 35.5″	1.5027
Fraction 2	0.9108	2′ 36.9″	1.5102
Fraction 3	0.9428	7′ 11.7″	1.5257
Gilsonite Distillate:			
Fraction 1	0.8552	1′ 26.2″	1.4753
Fraction 2	0.8827	2′ 48.4″	1.4854
Fraction 3	0.8919	3′ 23″	1.4928

The viscosities run parallel with the gravities and molecular weights. This shows, since viscosity is as a rule not dependent or conditioned by gravity, that all the constituents of all the different fractions of the asphalts belong to similar series of compounds, since the viscosities increase with the gravities and boiling points.

C. Index of Refraction.—The refraction measurements were made with an Abbé refractometer. The temperature at which these determinations were made was 20° C., and was kept constant within 1° C. The results are recorded in Table II.

The indices of refraction thus run parallel with the specific gravities of the oils, therefore (as will be shown later), the highest indices and gravities must also show the highest molecular weights.

Summary of Physical Constants.—The specific gravity, as mentioned above, is characteristic of the chemical nature of the oil. The nature of the oil is the summation of the properties of the individual components. Now oils that are high in paraffins give the lowest gravities. Hence, the asphalt distillates must be largely free from paraffins because of their high gravities. The gravities would indicate that asphalt distillates consist mainly of cyclic and unsaturated hydrocarbons, because hydrocarbons with a low hydrogen content would give high gravities.

As a rule the color of petroleum changes with the gravity, and

the intensity increases with the gravity. The asphalt distillates show the property, but since no sharp fractions were made, the differences in color are not great.

The viscosity of the fractions from petroleum increases with the rise in the boiling point, and this too is true with the asphalt oils. The different classes of hydrocarbons have different viscosities and a mixture of these would vary the viscosity so that it would not be strictly an additive property.

With increasing boiling point and increasing specific gravity the index of refraction rises. The indices of refraction of the asphalt distillates would indicate hydrocarbons of high molecular weights.

The similarity of the physical constants of the distillates shows that the asphalts studied break down in the same manner upon distillation.

Carbon and Hydrogen

The carbon and hydrogen content of each fraction of the different distillates were made by the combustion method.

The purpose of the combustions was to see in what manner the different fractions of the various asphalt distillates differed from each other, and how they compared with the original asphalts.

The procedure followed in making the combustions (carbon and hydrogen determinations) is that outlined in Fisher's "Laboratory Manual of Organic Chemistry."[23] The combustion tube was filled with copper oxide, cerium dioxide catalyst, lead chromate and a silver spiral. The substance was burned with lead chromate in an atmosphere of pure oxygen.

The samples analyzed were made moisture-free by shaking with freshly fused calcium chloride (fused calcium chloride was heated to a molten condition).

0.1500 to 0.2000 g. samples were analyzed. No difficulty was experienced in the combustion analyses.

Table III gives the average of two duplicate results. All combustions were run in duplicate, and all carbon determinations checked within 5 parts per thousand, and those of hydrogen within 15 parts per thousand.

The pure bitumen for the above analysis was obtained by dissolving the asphalts in C. P. chloroform. The solutions, after being allowed to stand long enough for all suspended matter to settle out, were decanted through cotton filters and finally

[23] See also Peckham, *J. Soc. Chem. Ind.*, **1897**, p. 996.

were filtered through a Gooch crucible with an asbestos pad. The filtrate was evaporated to dryness on a water bath. The bitumen thus obtained was dried in an oven at 100° C.

In examining the experimental results obtained from the combustions of the various asphalt distillates, it will be noticed that the results for all fractions were about alike. Not only did the different fractions obtained from the same asphalt show the same percentage of carbon and hydrogen, but this was also true of the fractions obtained from different asphalts. Thus the distillates obtained by the destructive distillation of Trinidad, Bermudez and Gilsonite asphalts show the same carbon and hydrogen ratio. The carbon-hydrogen ratio groups these oils with petroleum. It would therefore seem that destructive distillation of asphalt is not only a decomposition, but largely a depolymerization, and that the mechanism of the depolymerization is the same for the three asphalts.

TABLE III

ANALYTICAL RESULTS

		Carbon %	Hydrogen %
Trinidad Distillate:	Fraction 1	83.54	10.34
	Fraction 2	82.42	10.71
	Fraction 3	82.89	11.31
Bermudez Distillate:	Fraction 1	83.50	11.59
	Fraction 2	84.44	11.43
	Fraction 3	84.46	11.01
Gilsonite Distillate:	Fraction 1	84.87	12.57
	Fraction 2	84.83	12.07
	Fraction 3	85.00	11.83
Trinidad Pure Bitumen		74.22	8.62
Bermudez Pure Bitumen		76.78	8.68
Gilsonite Pure Bitumen		85.63	10.43

The fractions analyzed are not individual compounds, but mixtures of many compounds. Yet the analytical results compare well with those reported by Völckel and Kayser mentioned above, who assigned definite formulae to the asphalts they examined. These two investigators also found that the carbon and hydrogen ratio was about the same for the fractions they studied, which were taken at different temperature intervals than those studied in this research. Kayser's results differ slightly from those of Völckel. Kayser found that the last fractions had a higher percentage of carbon and less hydrogen than the first fractions; nevertheless, the differences are slight. This explained the increasing specific gravities of the oils with rise of temperature. Völckel's results do not account for the

rise in gravity and so have been rejected by previous workers.[24] The reason Kayser's results differ from those of Völckel is because Kayser had more fractions (ten in all) and so it is to be expected that the carbon ratio would increase. Kayser's results are correct; but so are Völckel's.

Effect of Distillation on the Sulphur Compounds of Asphalts

The purpose of the sulphur determinations was to find out how the destructive distillation affected the sulphur content of the asphalts and to what extent, if any, the sulphur content of the various distillates had affected the chemical and physical properties of the oils.

The sulphur determinations were made in a Parr Oxygen Bomb Calorimeter. Half-gram samples were burnt with oxygen at 325 pounds pressure. The sulphur was weighed as barium sulphate. Other details of the procedure were those of the standard method of sulphur determination. No analytical difficulties were experienced.

The following table gives the average of very closely checking duplicates:

	% Sulphur
Gilsonite, Selects, Pure Bitumen	0.78
Trinidad Lake Asphalt, Pure Bitumen	4.63
Bermudez Lake Asphalt, Pure Bitumen	4.16
Gilsonite Distillate, Fraction 1	0.46
Gilsonite Distillate, Fraction 2	0.25
Gilsonite Distillate, Fraction 3	0.20
Bermudez Distillate, Fraction 1	2.42
Bermudez Distillate, Fraction 2	2.76
Bermudez Distillate, Fraction 3	2.75
Trinidad Distillate, Fraction 1	2.92
Trinidad Distillate, Fraction 2	2.81
Trinidad Distillate, Fraction 3	2.72

Asphalts contain sulphur compounds and when distilled give off H_2S and other gaseous sulphur compounds and yield a fluorescent petroleum oil. But all the sulphur in the asphalt is not split off as hydrogen sulphide for the above analyses show that the oil continuously contains sulphur. Only a small portion of the sulphur splits off as hydrogen sulphide and other compounds; the remainder is combined and distills over as oil.

An examination of the above results shows that Trinidad distillates contained more sulphur than those from Bermudez, and the Gilsonite distillates the least of all. It is also shown

[24] Köhler-Graefe, "Die Chemie u. Technologie d. Natürlicken u. Künstlichen Asphalte," p. 89.

that the first fractions in each case contained the largest percentage of sulphur and that the third fractions contained the least. In the case of Bermudez distillates, the first fraction contained the least sulphur, but this peculiarity is readily explained by the fact that Bermudez asphalt contains a large quantity of unchanged petroleum,[25] and this distills over in the first fraction.

In the case of the physical constants—specific gravity, viscosity and the index of refraction—the smallest magnitude was always found in the first fractions and the largest in the third fraction. The sulphur magnitude runs in the reverse order. Therefore, it is concluded that the sulphur content does not determine the physical constants.

Later, in the case of the action of sulphur chloride on the distillates, it will be shown that the sulphur content affects the chemical nature of the oils.

Kayser[26] distilled a Trinidad asphalt containing 10% sulphur. The oil obtained was then redistilled into ten different fractions. He obtained a decreasing sulphur content which confirms the above results.

Petroleum also contains sulphur but when distilled, unlike in the case of asphalt, the sulphur content of the distillates increases with the boiling point and specific gravity.[27]

The information obtained from a study of the sulphur contents of the asphalts and their distillates also points to depolymerization.

Classification of Chemical Constituents

The distillates from the various asphalts were tested for phenols by the method used for phenol determination in coal tars.

A definite quantity of oil was shaken with a saturated solution of sodium carbonate in a Tar-Acid Separatory Funnel,[28] Type 1 (to remove carboxylic acids). After standing, the sodium carbonate solution was drawn off and the contraction in volume of the oil was read. The contraction in volume denoted the volume of carboxylic acids present in the oil.

The oil which was freed from carboxylic acids was treated with a 10% solution of sodium hydroxide to obtain the phenols.

[25] Marcusson, "Die Natürlichen und Künstlichen Asphalte," p. 23.

[26] Köhler-Graefe, "Die Chemie u. Technologie d. Natürlichen u. Künstlichen Asphalte," p. 90.

[27] Engler-Höfer, "Das Erdöl," Vol. I, p. 464.

[28] See "Apparatus Used in the Coal-Tar Industry," Empire Laboratory Supply Company, p. 46.

The test was carried out in the same manner as in the case of the carboxylic acids. Three extractions were made, using about 30 cc. for the first extraction and 20 cc. for each of the two following. The contraction in volume of the carboxylic acid free oil indicated the volume of phenols present. The phenols were in the sodium hydroxide solution and were in the form of sodium phenolates. They were isolated by acidifying with a 20% solution of sulphuric acid.

Although there was practically no contraction of volume of oil, there was nevertheless a slight reaction with Na_2CO_3 and the NaOH. First of all, the extractions were colored. When the Na_2CO_3 extract was acidified, a scum was precipitated which had the appearance and odor of the acids obtained by Marcusson's method on the original asphalts. That the asphalt distillates show reaction with sodium carbonate solution is in harmony with the fact that when asphalts are distilled the first few cc. are more acid than the succeeding.[29]

When the NaOH extract was acidified with sulphuric acid a scum was precipitated which had a phenolic odor. A test for phenols was made by extracting the acidified solution with benzine. The benzine solution was treated with sulphuric acid and formaldehyde. A pretty red coloration was obtained which proved the presence of phenols. A blank test was made on the benzine and no coloration was obtained. All distillates gave traces of phenols.

Since only a trace of phenols was present in the asphalt distillates the attempt was made to find out if phenols would form when the oils were heated for a long time. This experiment was carried out by refluxing the oil for several hours. The oil for this test was that obtained by distilling Bermudez Lake asphalt. The fraction distilling over between 310–200 (evidently a cracked product) was then redistilled. The oil thus obtained had a boiling point of from 110 to above 360° C. The oil was heavy as is the case with all the high fractions.

Seventy-seven cc. of this phenol-free oil were refluxed for 3 hours. No charring of the oil took place. After cooling the oil was tested for phenols. No contraction took place upon treatment with Na_2CO_3 and NaOH. Acidification of NaOH extract produced no phenolic odor and no scum precipitate. Hence phenols were not produced by refluxing.

Pyridine Bases.—The distillates of the various asphalts after treatment with sodium carbonate and NaOH to extract phenols (see the above phenol experiments) were shaken with a

[29] Marcusson, *Chem.-Ztg.*, **1912,** 802.

20% solution of sulphuric acid. These extractions were carried out in the same manner as for phenols. The sulphuric acid extracts were then made alkaline with NaOH solution to precipitate the pyridine bases. The pyridine bases were isolated from the NaOH solution by extracting with ether. After evaporating the ether solution a red liquid residue was left which contained the pyridine bases. They were identified as such by their odor and by the A. W. Hofmann test.[30] Only a trace of pyridine bases was found in the asphalt distillates.

Formolite Reaction.—Formaldehyde and sulphuric acid react with unsaturated cyclic hydrocarbons to form an insoluble precipitate. This precipitate is called "formolite."[31] This reaction gives a positive method of separating paraffines, olefines and cyclic hydrocarbons from the unsaturated cyclic hydrocarbons (benzene series and naphthylenes and polynaphthylenes). This reaction is known to be positive only for the lower members of the homologous series. Its reliability for the highest members has not been determined. Nevertheless, it is used to test for these members.

The formolites are yellow, amorphous compounds containing sulphur, oxygen, carbon and hydrogen. The constitution is not known. The test was made according to Marcusson's[32] modification which consists in dissolving the oil in benzine.

The asphalt distillates reacted with the sulphuric acid and formaldehyde to such a great extent that it seemed that the oil consisted for the most part of unsaturated cyclic hydrocarbons.

Asphalts are saturated cyclic compounds, as shown by Marcusson, and so if the distillates are also cyclic, as shown by the formolite reaction, this would be in keeping with the theory that asphalts largely depolymerize upon distillation.

Sulphuric Acid Test

It seemed desirable to know something about the nature of the hydrocarbons in asphalt distillates. In studying the literature, three methods seemed suitable for the purpose. The first was the action of mercuric acetate, the second was the liquid sulphur dioxide method of separating saturated hydrocarbons from the unsaturated, and the third method was the action of concentrated sulphuric acid on the unsaturated hydrocarbons.

Mercuric acetate reacts with unsaturated hydrocarbons and

[30] Rosenthaler, "Nachweis organischer Verbindungen."

[31] Nastjukow, *Z. anal. Chem.*, **46**, 257 (1907).

[32] Marcusson, *Chem.-Ztg.*, **1911**, No. 35, 729, and **1913**, No. 37, 533 and 550.

liberates some acid. This reaction was worked out as a quantitative method by Tausz.[33] Mercuric acetate also reacts with phenols and sulphur compounds, both of which are present in the asphalt distillates. Since different amounts of sulphur are present in the various fractions the mercuric acetate reaction could not be used to determine the relative amounts of unsaturated hydrocarbons in the various oils.

The Edeleanu process of separating saturated hydrocarbons from unsaturated ones was used on the second fraction of Trinidad asphalt. Twenty-five cc. of oil were treated with about 200 cc. of liquid sulphur dioxide. At first a smaller quantity of this reagent was used but the solution proved too viscous and so more had to be used. No separation was obtained, but an emulsion formed on top the sulphur dioxide and oil solution. At −25° C. this emulsion froze solid. The emulsion was washed with caustic soda and water and was then treated with sulphuric acid. It proved to consist of 25% saturated hydrocarbons. The oil dissolved by the sulphur dioxide was black like the original oil and had the same odor. About 12 cc. of oil were dissolved by the liquid sulphur dioxide. The emulsion also produced about 12 cc. of oil. In both cases, however, these volumes dwindled considerably before the oils were obtained in a purer form. The emulsion, it should have been stated, turned out to be an oil on washing with caustic soda. The color was somewhat yellow. This yellow oil was centrifuged at 2000 R. P. M. for twenty minutes to separate out the water and thus a reddish oil was obtained which gave the above-mentioned 25% saturated compounds. The portion soluble in the sulphur dioxide was not further treated. This method did not work well and no quantitative separation of the oil was obtained. The method was therefore abandoned for the sulphuric acid test.

The following procedure was used in the sulfuric acid test: 5 cc. of oil were placed by means of a standardized pipette in a Babcock oil bottle which read percentage directly within 0.5%. (When 5 cc. of oil are used the percentage must be multiplied by 2, since the bottle only reads to 50%.) Ten cc. conc. sulphuric acid were then added and the bottle was set in cold water with occasional shaking until no more heat was developed. Then enough concentrated sulphuric acid was added to fill the bottle up to the neck. The Babcock bottle was then centrifuged for three minutes at 1000 R.P.M. The bottle was then taken out of the centrifuge, and the neck was filled almost to the top

[33] Berl, *Ber.*, 1912.

with concentrated sulphuric acid. Then it was centrifuged again, but this time for five minutes. The amount of saturated hydrocarbons was read off directly in per cent. and multiplied by 2. The following results were obtained:

Name		Saturated hydrocarbons %
Trinidad Distillate	Fraction 1	50.0
Trinidad Distillate	Fraction 2	39.0
Trinidad Distillate	Fraction 3	38.0
Bermudez Distillate	Fraction 1	60.0
Bermudez Distillate	Fraction 2	53.0
Bermudez Distillate	Fraction 3	49.0
Gilsonite Distillate	Fraction 1	63.0
Gilsonite Distillate	Fraction 2	54.0
Gilsonite Distillate	Fraction 3	48.0

The above results are accurate to 0.5%. No difficulty was encountered in the use of the method. It is here shown that the Trinidad distillates contained the smallest, and those of the Bermudez and Gilsonite the greatest amounts of saturated hydrocarbons. The hydrocarbon content of the Bermudez and Gilsonite distillates were about equal. In all cases the first fraction showed the highest percentage of saturated hydrocarbons and the third fraction the lowest.

The great similarity of the various asphalt distillates in their degree of unsaturation again points to depolymerization in distillation of asphalts. That asphalt distillates are highly unsaturated is of importance in connection with the study made of the action of sulphur chloride on their oils.

The evidence so far presented seems to indicate rather definitely that all of the asphalt distillates studied are very similar in composition. They are highly unsaturated and contain traces of phenols and pyridine bases. The formolite reaction shows them to be composed largely of unsaturated cyclic hydrocarbons.

Molecular Weights

It seemed desirable to investigate the molecular magnitude of asphalts and the oils obtained by their destructive distillation. The only feasible method for the molecular weight determination is the Beckmann Freezing-Point Method, since in all other methods heating is required and this would decompose the oils. The method was carried out as described in standard textbooks.[34]

[34] Ostwald-Luther, "Physiko-Chemische," Messungen and Findlay, "Practical Physical Chemistry."

The method offered very little difficulty and sharp temperature readings could be made. At the concentrations used there was no evidence of association of molecules. The temperature was read to 0.001°. The weight of the solvent (benzene) was known to 0.01 gram.

The molecular weights found are tabulated below, and represent the average of two closely checking duplicate determinations.

Trinidad Bitumen	1131.8
Bermudez Bitumen	620.4
Gilsonite Bitumen	4251.5

Name		Molecular weight
Trinidad Distillate	Fraction 1	228.9
Trinidad Distillate	Fraction 2	238.8
Trinidad Distillate	Fraction 3	227.0
Bermudez Distillate	Fraction 1	224.9
Bermudez Distillate	Fraction 2	220.7
Bermudez Distillate	Fraction 3	282.5
Gilsonite Distillate	Fraction 1	203.7
Gilsonite Distillate	Fraction 2	223.2
Gilsonite Distillate	Fraction 3	226.3

It should be noted that the molecular weights as determined by the Freezing-Point Method run parallel to the specific gravities of the oils. A slight peculiarity is found in the Bermudez distillate No. 2, but this is probably due to the prevalence of certain hydrocarbon series which would tend to prevent the carbon-hydrogen ratio from being additive. In the case of Trinidad distillates No. 3, the result came out lower than expected. This is due to the ratio of the different hydrocarbons present and to the fact that the third fraction is highly cracked.

It will also be noticed that all the molecular weights of the asphalt distillates are of about the same magnitude. This is in accordance with the fact that all the distillates have the same percentage of carbon and hydrogen.

That asphalts when destructively distilled should give oils that have the same percentage of carbon and hydrogen and the same molecular weights shows that the asphalts do not merely decompose, but that they are largely depolymerized.

The molecular weights of the original asphalts are very much greater than those of the distillates. The determination of the molecular weight of Gilsonite proved to be difficult, because the temperature depression is so small. Gilsonite has the largest molecular weight and Bermudez the smallest. This is ex-

plained by the work of Marcusson[35] who found that Bermudez asphalt contained the most unchanged petroleum, Trinidad less, and Gilsonite least of all. It is also concluded from the molecular weight determinations that Gilsonite is made from lighter oils than is Bermudez and Trinidad, because the Gilsonite distillates are lighter and of smaller molecular magnitude. The reverse is also true, namely, that Gilsonite is the most polymerized asphalt, Trinidad is next and Bermudez last. That Bermudez asphalt is the least polymerized is shown by its molecular weight and by the high percentage of saturated hydrocarbons in the distillates and by the unchanged petroleum in the original asphalt.

Action of Sulphur Chloride on Asphalt Distillates

(a) **Qualitative.**—In the previous experiments it was shown that all of the asphalts examined break down in the same manner, and it was concluded that depolymerization took place and not decomposition alone, as the splitting off of hydrogen sulphide would indicate. Inasmuch as the oils were depolymerization products, it was desired to know if they could again be polymerized by the action of a polymerizing agent. The polymerizing action of sulphur chloride on rubber suggested that it might be a useful reagent for this purpose.

The preliminary attempts to vulcanize the asphalt distillates with sulphur chloride were not successful. A reaction took place but the resulting product was not satisfactory, the oil simply gumming and forming a brittle mass. In one case, however, a product was obtained that could be drawn out into long rubber-like strings. At first the elasticity was small, but upon standing the substance became harder and also more ductile. These properties were first noticed 24 hours after the addition of sulphur chloride to the oil. The proportions of oil and sulphur chloride were not known.

An attempt was therefore made to learn the exact conditions under which such ductile material could be produced. To 20 cc. of the second fraction of the Trinidad asphalt distillate 3 cc. sulphur chloride were gradually added with stirring. Later this was done with each of the three fractions obtained by distilling Refined Trinidad Lake asphalt. Upon addition of the sulphur chloride a portion of the material coagulated and settled out. When an excess of sulphur chloride was added, the coagulated mass dissolved converting the whole mass into

[35] Marcusson, *Z. angew. Chem.*, **1916**, p. 346.

a frothy liquid. Much heat was generated and hydrogen chloride was evolved.

After standing 48 hours the products of this reaction were viscous liquids in all three cases. The ductile, asphalt-like material sought had not been produced. It was then thought that different concentrations of sulphur chloride might yield different results; accordingly the above experiments were repeated, using 20 cc. oil and 20 cc. sulphur chloride. Different results were obtained. The products, after remaining liquid about ten days, gradually became solid. The reason for remaining liquid was that an excess of sulphur chloride kept the products in solution.

In subsequent experiments less sulphur chloride was tried: 10 cc. of the reagent and 20 cc. of oil were used. After standing over night a rubber-like product was obtained. It therefore seemed that 10 cc. of sulphur chloride to 20 cc. of oil represented the proper reaction proportions and this ratio was used in all subsequent experiments on the various asphalt fractions.

In each case, when the sulphur chloride was added to the oils, a violent reaction resulted, much heat was produced, hydrogen chloride was given off and a frothy black liquid was obtained which, after standing over night at room temperature, became solid.

The experimental results obtained on the different fractions are grouped and described in the following table, under the particular asphalts from which they were obtained.

Name	Fraction 1	Fraction 2	Fraction 3
Trinidad Distillate:	Black solid product, with some liquid. No ductile material.	Black solid product. No liquid. Ductile product.	Black solid product, harder than No. 2. Ductile.
Bermudez Distillate:	Black solid product. Some liquid. No ductile material.	A black solid. Ductile, but softer than Trinidad No. 2. No liquid.	Black solid. No liquid. Ductile, but softer than Trinidad No. 3.
Gilsonite Distillate:	Black solid. Some liquid remained. No ductile material.	A black ductile material. No liquid remained. Similar to Bermudez No. 2.	Black solid and ductile. No liquid remained. Similar to Bermudez No. 3.

Upon continued standing, all of these products became gradually harder and lost the property of ductility, a fact which at the time seemed to have little significance, but which later was found to be of considerable importance. It was first thought that the loss of ductility was due to further action of the sulphur chloride, but, as will be shown later, it was due to a chemical transformation of the sulphurated products.

Although the action of the sulphur chloride on all of the fractions was similar, however, perceptible differences in the properties of the products were noted.

Solvent Action on Vulcanized Products.—The asphalt distillates are all soluble in benzene, carbon disulphide, petroleum ether, dichloroethylene[36] and carbon tetrachloride.

All the above-described sulphurated or vulcanized products are very readily soluble in carbon disulphide, but less readily in carbon tetrachloride. In petroleum ether they are practically insoluble.

Conclusions

Probably the best way to describe the products obtained when asphalt distillates are treated with sulphur chloride is to say that the oil has reverted back to asphalt. This, in fact, seems to be what really happens. It is therefore believed that dry distillation depolymerizes asphalt, and that the oils thus obtained when sulphurated revert back again to asphalt.

It is further believed that the reaction takes place in two stages. First, the sulphur chloride reacts with the oil forming froth and giving off hydrogen chloride, thus forming sulphur compounds with the oil. Then, upon standing, these sulphur compounds polymerize and form black solids which are largely insoluble in petroleum ether and are therefore asphaltenes.

(b) **Quantitative.**—Since the qualitative study of the action of sulphur chloride gave such valuable information, it seemed desirable to have a quantitative expression of the reaction.

The method used for the quantitative measurement of the action of sulphur chloride on asphalt distillates was that of Meigs.[37] The method consisted of absorbing the hydrochloric acid gas evolved in the reaction between sulphur chloride and the bitumen in water and titration with $N/20$ NaOH solution. The procedure and apparatus are fully described in Meigs' article.

Meigs suggests the use of methyl orange as indicator, but it was found that it does not work well. A sharp end-point could not be obtained. Besides methyl orange does not work satisfactorily in $N/20$ alkali solutions, but it should be used in $N/5$ and stronger solutions. Meigs even suggests the use of $N/50$ NaOH with methyl orange. But since no results could

[36] Mentioned here for the first time. A mixture of cis and trans. Dissolves asphalts in the same degree as chloroform.

[37] *J. Ind. Eng. Chem.*, **9**, 655 (July, 1917).

be obtained with methyl orange, phenolphthalein was used as indicator and it gave excellent results.

The results are expressed as a "hydrogen number," namely, 100 × milligrams of hydrogen removed from organic combination and evolved as hydrochloric acid gas by the "oxidizing action"[38] of sulphur monochloride as one gram of the substance examined. Expressed in terms of sodium hydroxide solution, we have the following formula for the "hydrogen number," *viz.*:

$$\frac{\text{cc. NaOH solution} \times N}{\text{Weight of sample}} \times 100 = \text{Hydrogen number}$$

where N equals normality of the sodium hydroxide, preferably $N/20$. From 0.2 to 0.5 g. of asphalt distillate and 10 cc. of the sulphur monochloride reagent described in Meigs' article were used. The sample was first dissolved in 15 cc. of carbon disulphide before the sulphur chloride solution was added.

The following results were obtained (each is the average of two closely checking results):

Name		Hydrogen number
Trinidad Distillate	1	163.5
Trinidad Distillate	2	261.1
Trinidad Distillate	3	344.9
Bermudez Distillate	1	59.7
Bermudez Distillate	2	133.5
Bermudez Distillate	3	287.5
Gilsonite Distillate	1	626.0
Gilsonite Distillate	2	956.8
Gilsonite Distillate	3	978.6

A single analysis takes four hours and is, therefore, very tedious and time-consuming. A study of the results obtained shows that the higher fractions gave the highest "hydrogen numbers." The first fractions gave the lowest and the third fractions the highest "hydrogen numbers." Among the different varieties of asphalts the distillates of Gilsonite gave the highest hydrogen numbers and those of Bermudez Lake the lowest, whereas those obtained from Trinidad Lake fall between.

(c) **Analysis of Asphaltenes.**—When asphalts are destructively distilled fluorescent oils are obtained as distillates. As stated previously, when mixed with sulphur chloride these oils polymerize and are converted into solid substances. The solid substances are soluble in chloroform, benzol and carbon bisulphide; but largely insoluble in petroleum ether.

[38] Meigs, *J. Ind. Eng. Chem.*, **9**, 655 (July, 1917).

On the basis of these solubilities a method is proposed to determine quantitatively the action of sulphur chloride on asphalt distillates in the formation of asphaltenes.

For analysis 20 cc. of the asphalt distillate (Trinidad) were treated with 10 cc. sulphur chloride. The mixture was allowed to stand over night and then dissolved in about 20 cc. benzene. The benzene solution was poured into 20 cc. of petroleum ether. The petroleum ether solution was decanted and the precipitate again dissolved in benzene and precipitated by petroleum ether. This procedure was repeated three times to get rid of the free sulphur chloride. The precipitate (asphaltenes) was then dried on a water bath and analyzed for sulphur in a Parr Oxygen Bomb Calorimeter. The analysis gave 35.15% sulphur.

The above method worked well with the exception that the sulphurated product is somewhat soluble in petroleum ether and so a strictly quantitative precipitation could not be obtained. Furthermore, it was found that the petroleum ether insoluble material increased in amount if allowed to stand over night. This shows that a slow transformation is taking place. Nevertheless, the method worked well for the analysis of the asphaltenes.

(d) **Transitions.**—When the sulphurated product was dissolved in benzene and then precipitated with petroleum ether, and when the petroleum ether solution was decanted off and evaporated, a heavy black oil was obtained. When this procedure was repeated, the second petroleum ether extract gave a very viscous and almost solid product upon evaporation. When the "asphaltenes" were extracted for the third time with petroleum ether, a still more viscous product was obtained. The "asphaltenes" after the three extractions became quite hard. After standing, the petroleum ether residues slowly lost their solubility in petroleum ether and formed asphaltenes.

(e) **Marcusson's Method.**—When the above transitions were noticed Marcusson's scheme of asphalt analysis was tried. The oil was sulphurated with sulphur chloride and allowed to stand over night. It was then dissolved in a small quantity of benzene and poured into 200 cc. of petroleum ether. Asphaltenes were precipitated. The petroleum ether was decanted and evaporated to small volume and poured over fullers' earth in a Soxhlet thimble where it was extracted first with petroleum ether to obtain the unchanged oils, and then with chloroform to obtain the asphaltic resins.

Thus it was shown that sulphuration of the asphalt distillates produced unchanged oils, asphaltic resins and asphaltenes.

The "synthetic" unchanged oils gave the same index of refraction (1.449) as those obtained from natural asphalt (Trinidad). The resins did not agree in the index of refraction. This is undoubtedly due to the fact that the action of sulphuration cannot be exactly controlled.

The synthetic asphaltenes, unchanged petroleum and asphaltic resins are, like those of the natural products, convertible into each other.

(f) **Asphalt Binder.**—Since the sticky, ductile, synthetic asphaltic resins were so readily converted into asphaltenes, it was thought that they might be the "binder" material of asphalts. That they furnish the elastic properties of asphalts has been known. To determine whether or not they formed the "binder" substance, pure asphaltic resins, both synthetic and natural, were exposed to the air until a black powder was obtained. This was also done in another manner.

Asphalts (on roads) become brittle or rather they "dust off," especially when under a pool of water. This is due to the oxygen dissolved in the water. The oxygen slowly oxidizes the asphaltic resins to asphaltenes. The elastic ductile material in vulcanized oils was placed under water and it formed black dust which proved the manner of disintegration of paving asphalt.

These experiments showed definitely the similarity between the synthetic and natural asphaltic resins, and gave rather conclusive evidence in support of the conclusion that they are the binder material in asphalts.

(g) **Sulphuration of Crude Petroleum.**—Texas, Oklahoma and Louisiana crude petroleums were treated with sulphur chloride in carbon tetrachloride solution. No reaction ensued nor was any heat evolved.

In the case of shale oil a violent reaction ensued and asphaltic material was formed which was insoluble in petroleum ether. The shale oil was highly unsaturated, the crude petroleums were not. These reactions, therefore, show that the action of sulphur chloride is largely a measure of unsaturation.

Summary of All Experiments

The physical constant determinations show that the different fractions vary slightly in their specific gravity, viscosity and index of refraction. Yet there is a great similarity in these constants. The first fractions give the lowest and the third fractions the highest values for the constant.

The reason the physical constants varied as they did was

shown by the sulphuric acid test. This test showed that the first fractions were the most highly saturated, and the third fractions the least. The third fraction would, therefore, be expected to have the greatest specific gravity, which is the case for each of the asphalts. That the Trinidad distillates all possess higher specific gravities than those of the other asphalts is likewise due to the fact that they are more unsaturated. The Gilsonite distillates are the most saturated, and so have the lowest specific gravities.

The carbon and hydrogen determinations showed that all the distillates had about the same composition. The carbon-hydrogen ratio was around 83:11 in each case. All of the asphalts examined broke down in the same manner. The distillates gave the formolite reaction which undoubtedly is evidence of the presence of unsaturated cyclic hydrocarbons.

That these oils should give about the same percentages of carbon and hydrogen was confirmed by the molecular weight determinations. The molecular weights ran parallel with the specific gravities as was to be expected. An examination of all the molecular weights showed they were all of a similar magnitude.

The first fractions of all of the distillates possessed the highest percentages of sulphur, while the third fraction possessed the lowest, the inverse of the specific gravity values. Trinidad distillates contained the most sulphur, and Gilsonite distillates the least.

The quantitative measurements of the reactions between sulphur chloride and the asphalt distillates showed that the sulphur chloride reacted with the unsaturated compounds. The Trinidad distillates were more unsaturated than the Bermudez and so gave higher "hydrogen numbers." The Gilsonite had the highest hydrogen number, but it is slightly less unsaturated than Bermudez. This peculiarity is accounted for by the presence of sulphur. The Gilsonite oils had only a small amount of sulphur. The first fractions of all the oils gave the lowest "hydrogen numbers" because they were the least unsaturated; the third fractions gave the highest because they were the most unsaturated.

Meigs in his article did not know whether the "hydrogen number" was a measurement of the unsaturated compounds or not. There seems to be sufficient evidence now for the belief that the sulphur chloride reacts with the unsaturated compounds quantitatively, and that if the reaction is properly controlled it may be used to determine the extent of unsatura-

tion in oils of this type. This was also shown by the fact that sulphur chloride did not react with pure naphthenes, and that when sulphur is already present in the molecule it decreases the extent of the reaction.

The qualitative reaction with sulphur chloride also brought out this fact. It was found that the first fractions gave the least reaction with sulphur chloride.

The qualitative experiments also showed that the reaction took place in two stages: First, sulphur compounds were formed with evolution of hydrochloric acid gas; Secondly, after standing, the sulphur compounds polymerized and became solid.

The reaction with sulphur chloride also showed that asphalt constituents are formed. Thus the sulphurated distillates which were analyzed by Marcusson's method gave asphaltenes, asphaltic resins and unchanged petroleum. These synthetic constituents could be transformed into each other; thus, the unchanged oil was converted into asphaltic resins, and the resins into asphaltenes, which are hard and brittle. In this manner it was demonstrated that the resins form the "binder" material of asphalts. It was further shown that the resins could be oxidized by oxygen dissolved in water to asphaltenes, destroying the "binder" and the asphaltic properties of the material.

The similarity between distillates of all of the asphalts shows that they depolymerize in the same manner. The action of sulphur chloride shows that these distillates can again be polymerized.

The Mechanism of Asphalt Formation

In this research the formation of asphalts has been studied by the reaction of sulphur chloride on the asphalt distillates. It is held that the destructive distillation causes a depolymerization of the asphalts and asphaltites. The basis for this assumption is the similarity of the chemical and physical properties of the distillates. Furthermore, asphalts and asphaltites are of a cyclic character[39] and cyclic compounds admit of depolymerization.[40] The distillates, also, seem to be of a cyclic nature, since they give the formolite reaction.

Asphalts depolymerize on destructive distillation and it is also believed that sulphur chloride again polymerizes the distillates into asphalt.

When sulphur chloride acts on the asphalt distillates a violent

[39] Marcusson, *Z. angew. Chem.*, **1916,** p. 346.

[40] Engler-Höfer, "Das Erdöl," Vol. I, p. 421.

reaction ensues; after standing over night the liquid becomes a solid mass, which has the appearance and physical and chemical properties of asphalts, and, as shown above, is asphalt. Of course, no product identical with natural asphalt could be obtained, because the reaction of sulphur chloride is very violent and accordingly brings about some reactions which differ from those in actual asphalt formation.

That the sulphur chloride reaction takes place in two stages is also in harmony with the fact that the presence of sulphur in the hydrocarbon molecule does not alone produce asphalt or polymerization. Petroleum contains sulphur, yet this sulphur has no polymerizing action.

If asphalts consist of polymerized hydrocarbons in which sulphur is one of the polymerizing agents, then the asphalt molecule must be very large. That the molecule is very large was shown by Errera,[41] who found that the asphaltenes in natural asphalt had a very high molecular weight. Ultrafiltration showed that these sulphur compounds were colloidal. A molecular weight on "synthetic asphaltenes," obtained above by precipitation of the sulphuration product with petroleum ether, gave a molecular weight of 1409.7.

Analysis of the synthetic asphalt showed that it contained unchanged oil, asphaltic resins and asphaltenes. The synthetic unchanged oil gave the same index of refraction as that obtained from the natural asphalt. It was also found that these products readily changed into each other; thus the asphaltic resins changed into the petroleum ether insoluble asphaltenes Asphalts, therefore, are in a state of flux.

The sulphur chloride reaction seems to explain another fact Graefe[42] found that natural asphalts give off hydrogen sulphide and blacken lead acetate paper when heated to 200° C. Asphaltites do not, and this points to a difference in the combination of the sulphur in the asphalts and asphaltites. Even Syrian asphaltite with its high sulphur content does not give off hydrogen sulphide. The sulphur chloride reaction, therefore, leads to the belief that sulphur plays a double role in the formation of asphalts, and that it is present in two chemical combinations: (1) that which is held firmly in combination and goes over unchanged into the distillates, and (2) that which is loosely held and passes off in the form of hydrogen sulphide when the asphalts are heated. This sulphur is believed to be the polymerizing agent. In the case of asphaltites the sulphur is not

[41] Errera, *Trans. Faraday Soc.*, **19**, 314–317 (1923).

[42] *Z. angew. Chem.*, **1916**, p. 25.

the polymerizing agent, but oxygen is. So, when asphaltites are heated, hydrogen sulphide is not given off.

The presence of phenols and pyridine bases in the asphalt distillates merely points to the fact that asphalts have been derived from petroleum, since petroleum contains these substances.

The depolymerization and polymerization theory shows that the primeval oils from which Trinidad asphalts are formed are heavier than those of Bermudez. The Gilsonite, according to this, is built up from much lighter oils.

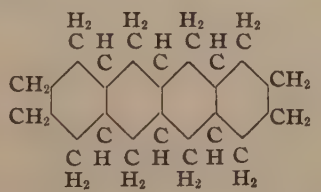
The quantitative measurement of the action of sulphur chloride on asphalt distillates shows that asphalt formation is due largely to the presence of unsaturated hydrocarbons. When sulphur is already present in the molecule the reaction is not so great.

Nellensteyn[43] considers asphalts to be elementary carbon which holds organic compounds by adsorption. This theory seems unreasonable, and is not in harmony with the above experiments.

Probable Structure of Asphalts.—The study of the mechanism of asphalt formation has shown that the asphalt molecule must be very large.

If the oil obtained by the distillation of asphalt is taken as the unit from which the asphalt molecule was built up, since asphalt depolymerizes on distillation, it is possible to speculate, and within the realm of possibility, as to the size of the asphalt molecule by a study of the molecular weights.

The average molecular weights of the hydrocarbons in the oils were about 228. This would suggest polycyclic compounds with about 4 rings:



This saturated compound has a molecular weight of 246. The oils, of course, are unsaturated and contain sulphur, but for the present purpose this may be neglected. The molecular weight of Trinidad asphalt was found to be 1131.8 and this would suggest that the asphalt molecule is about 3 to 4 times as large as the 4-ring polycyclic hydrocarbon, and so would contain about 12 to 16 rings. Since only the average molecular weights of the

[43] *Chem. Weekblad*, **21**, 102–106 (1924).

hydrocarbons of the asphalt distillates have been determined it follows that some of the hydrocarbons may be much larger than 4-ring compounds and some much smaller.

The size of the asphaltic molecule explains the great complexity of asphalts.

Summary

1. A systematic study has been made of the distillates of three representative asphaltic materials.

2. A new solvent was discovered for asphalt bitumen.

3. A determination of the physical constants and a study of the chemical properties of the distillates showed that asphalts largely depolymerize upon destructive distillation.

4. The study of the action of sulphur chloride on the distillates showed some of the mechanism by which asphalts might be formed.

5. The quantitative estimation of the sulphur chloride reaction showed that this reaction is a measure of the unsaturation of the hydrocarbons present. The presence of sulphur in the oil diminishes the magnitude of the reaction. The sulphur chloride reaction can be used for determining unsaturation.

6. On the basis of the experimental data it was shown that asphalts are depolymerized upon destructive distillation, and again polymerized when the distillation products are treated with sulphur chloride.

7. A new property is assigned to the asphaltic resins, namely: that of the "binder" material of asphalts. On the basis of this "binder" theory the deterioration of asphalt pavements has been explained.

8. The difference in sulphur combination in asphalt and asphaltite has been explained.

9. A new method has been developed for the analysis of synthetic asphaltenes.

10. A method is suggested by which the probable structure of the asphalt molecule may be calculated.

11. Analysis of the sulphurated asphalt distillates by Marcusson's method showed that synthetic products are formed and which are similar to the natural components of asphalts.

12. A study of the reaction of sulphur chloride with the asphalt distillates showed that sulphuration takes place in two stages: First, sulphur compounds form with evolution of hydrochloric gas and heat; secondly, after standing, the sulphur compounds polymerize and become solid.

13. Phenols and pyridine bases have been found to be

present in asphalt distillates. Phenols are not formed during destructive distillation of asphalts.

14. The study of the properties of the asphalt distillates showed that Trinidad asphalts are formed from heavier petroleum than either Bermudez or Gilsonite. Gilsonite is built up from lighter oil than is Bermudez.

This research was planned and carried out for the purpose of discovering fundamental information that would throw some light upon the mechanism of asphalt formation, with the hope that a knowledge of the constitution of asphalt would enable the manufacture of useful products for which asphalt was the important raw material.

It is believed that this research has thrown enough light upon the nature of asphalts and their distillation products to indicate rather definite lines along which additional research may be carried out for the production of new substances of commercial value from asphalts.

VITA

Ottomar G. Strieter was born in Frankenmuth, Cass County, Michigan, September 12, 1892. His primary and intermediate education was obtained in private schools. In August, 1915, he received the degree of Bachelor of Arts from the University of Nebraska. During the years 1915 to 1921 he was employed as chemist by the following firms: Stillwell & Gladding, Consulting Chemists, New York City; British-American Chemical Company, Manufacturing Chemists, Ridgefield Park, New Jersey; U. S. Air Nitrate Corporation, Plant No. 2, Muscle Shoals, Alabama; and the American Steel and Wire Company, Coke Plant, Cleveland, Ohio. He entered the Department of Pure Chemistry, Columbia University, in September, 1921, and received the degree of Master of Arts in 1922. Since 1922 he has been carrying on research on asphalts under the direction of the Department of Chemical Engineering, Columbia University.